ANALYSIS OF CYANIDE

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Cyanide Production:

Methane and ammonia react in the presence of oxygen at about 1200 °C over a platinum catalyst

$2\ CH_4 + 2\ NH_3 + 3\ O_2 \rightarrow 2\ HCN + 6\ H_2O$

Methane and ammonia are partially oxidized

In manufacturing, cyanide is used to make paper, textiles, plastics and is also present in the chemicals used to develop photographs.

Cyanide salts are used in metallurgy for electroplating, metal cleaning, and removing gold from its ore, as well as to recover gold from plating streams.

Only about 1/10th of the cyanide used each year is used for mining.

Industrial users of CN^- do pre-treat, so that influent levels are normally non-existent to very low…

Where does the cyanide in drinking and wastewater samples come from?

Difficulties

Cyanide levels are tested in drinking and wastewater.

According to the USEPA, the only method more challenging is that for Oil and Grease.

Cyanide chemistry is complex and matrix interferences can be very hard to identify and alleviate.

Treating for an interference can make things worse.

Some interferences have no known mitigation.

The number of interferences, along with required measurements in single part per billion ranges make distillation problematic.

Difficulties….

One of the most frustrating aspects of this analysis is that it is possible to have CN levels higher in the **effluent**, than they were in the **influent**!

Cyanide can even be generated in the water treatment process during disinfection (Chlorination and UV)

The methods suffer from multiple interferences that can cause cyanide to be created, or destroyed.

The very act of preserving the sample (as required) can in itself be problematic.

Interferences…

Adding NaOH to samples containing **formaldehyde**, an ozone disinfection byproduct, can possibly result in cyanide formation during storage (ES&T, Vol. 41, 2007, Delaney, M.F., et. al.)

Adding NaOH to samples containing **thiocyanate** in the presence of **chloramines**, which can form from ammonia and chlorine, can also result in cyanide formation during sample storage.

➡ The analytical issues many labs see are NOT due to human error, or poor sampling procedures… they are due to sample pre-treatment, storage and the conditions used in the distillation.

USEPA, Standard Methods, and ASTM all acknowledge the shortcomings in these methods.

Interferences

- ✓ Preservation with NaOH
- ✓ Sulfide and sulfur
- ✓ Aldehydes (formaldehyde, acetaldehyde)
- ✓ Oxidants-chlorine, hypochlorite, etc.
- ✓ Sulfite, thiosulfate, thiocyanate
- ✓ Carbonate
- ✓ Nitrate and nitrite
- ✓ Carbon compounds and nitrogen compounds in the sample (SAD cyanide)

A Study:

False cyanide formation during drinking water sample preservation and *storage*. Environmental Science &. Technology. 41: 8383-8387. Khoury et al. 2008.

The Massachusetts Water Resources Authority (MWRA) did a study on the effect of sample preservation and storage on the subsequent level of cyanide measured in the samples. This particular study relates ONLY to drinking water.

They split samples, then added formaldehyde to one aliquot of finished drinking water samples, (ozone/chloramination)

Samples were analyzed in triplicate following 3 different procedures.

1) Immediate distillation on site
2) Stabilized on-site in a MicroDist^{TM} tube, and distilled at the lab several days later, and
3) Conventional preservation (pH>12) followed by distillation at the laboratory.

ONLY the sample handled in the conventional, proscribed manner had detectable cyanide.

False cyanide formation during drinking water sample preservation and *storage*. Environmental Science &. Technology. 41: 8383-8387. Khoury et al. 2008.

The researchers found no detectable cyanide in any of the samples initially. They saw cyanide develop in the samples over time (2-10 days).

It did not matter if the sample had been dechlorinated, or if it had formaldehyde added to it.

36 samples were distilled immediately; 36 samples were stabilized in the MicroDist tubes. None of these samples had detectable cyanide.

False cyanide formation during drinking water sample preservation and *storage*.
Environmental Science &. Technology. 41: 8383-8387. Khoury et al. 2008.

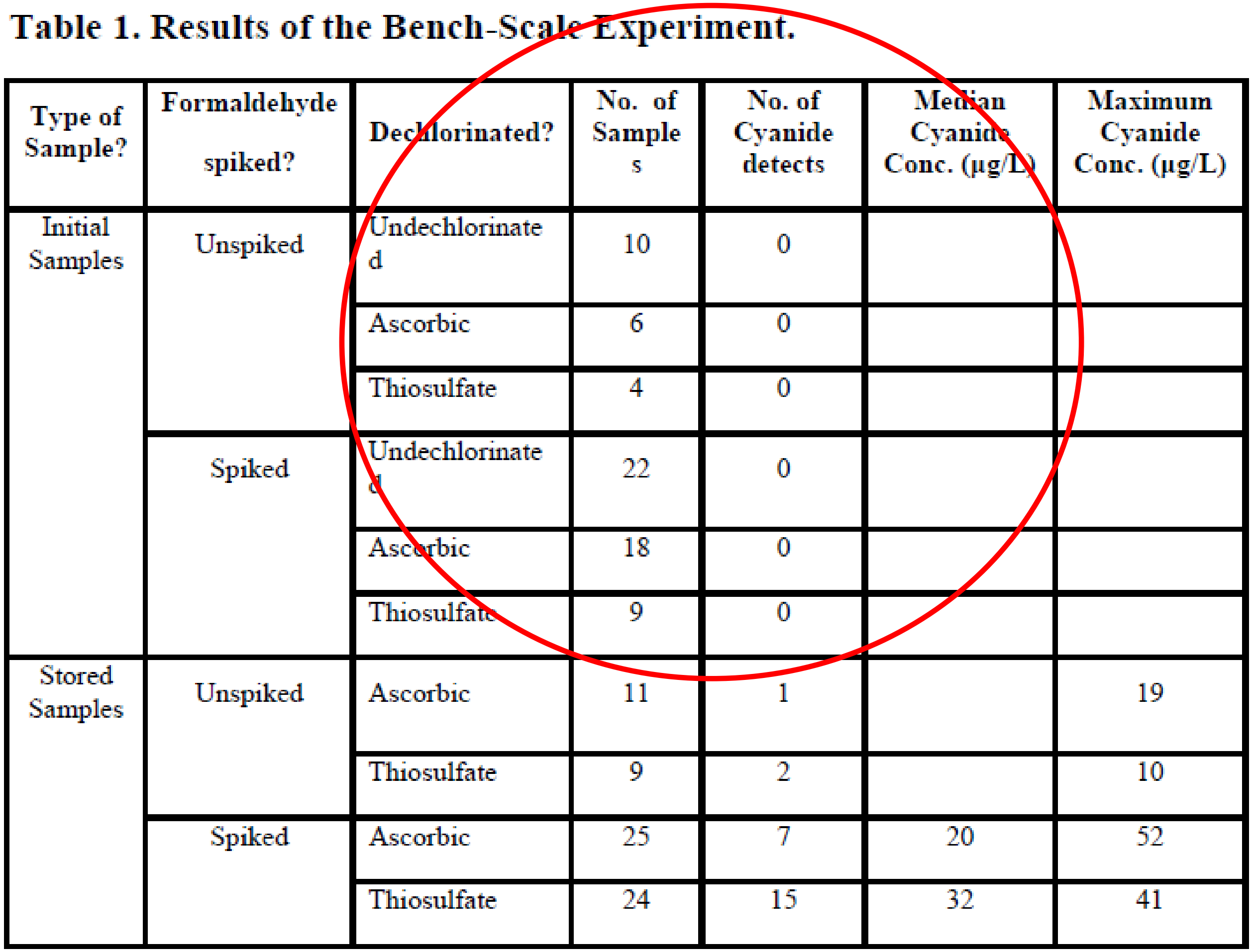

Table 1. Results of the Bench-Scale Experiment.

Type of Sample?	Formaldehyde spiked?	Dechlorinated?	No. of Samples	No. of Cyanide detects	Median Cyanide Conc. (µg/L)	Maximum Cyanide Conc. (µg/L)
Initial Samples	Unspiked	Undechlorinated	10	0		
		Ascorbic	6	0		
		Thiosulfate	4	0		
	Spiked	Undechlorinated	22	0		
		Ascorbic	18	0		
		Thiosulfate	9	0		
Stored Samples	Unspiked	Ascorbic	11	1		19
		Thiosulfate	9	2		10
	Spiked	Ascorbic	25	7	20	52
		Thiosulfate	24	15	32	41

False cyanide formation during drinking water sample preservation and *storage*.
Environmental Science &. Technology. 41: 8383-8387. Khoury et al. 2008.

Only the method for Oil and Grease is more problematic than that for Cyanide.

ASTM does have a standard related to mitigation of some of the issues. ASTM D 7365-09a *Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide*

This standard has additional information applicable to 40 CFR 136 CWA methods for testing of wastewater samples, and describes new procedures for preservation of samples

It can be purchased from ASTM International.

D7365-09a specifies that users should conduct a hold-time study prior to elimination of NaOH. Once the hold-time study is complete, NaOH may be omitted as a preservative as long as the sample is analyzed within the determined holding time.

EPA adds:

There may be interferences that are not mitigated by the analytical test methods or D7365- 09a.

Any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method.

Any removal or suppression technique not described in D7365-09a or the analytical test method must be documented along with supporting data.

CYANIDE ANALYSIS

Cyanide

Cyanide exists in a variety of forms.

It can be free or part of strong or weak complexes with other species, or a mixture of these.

Cyanide is regulated in drinking and wastewater.

Types of CN^- commonly measured include: total, available, amenable to chlorination, weak acid dissociable, and free.

Cyanide

- The sample preparation method used determines what fraction of CN is measured; <u>all CN measurements are method determined.</u>

DEFINITIONS

http://www.cyanidecode.org/
http://technology.infomine.com/reviews/Cyanide (You have to register to use this site)

General Overview:

TOTAL CN

Free Cyanide, acid-dissociale cyanides, and strong metal-cyano complexes such as ferri and ferro cyanide, hexacyanocobaltate, and gold and platinum cyanides

WAD CN

Free CN and weak metal cyano complexes such as cadmium cyanide, manganese cyanide, nickel cyanide, and mercury cyanide. This is basically equivalent to CATC (cyanide amenable to chlorination)

FREE CN

HCN and CN^- in solution

►For a given solution: ***<u>the total cyanide level is always greater than or equal to the WAD cyanide level, and likewise, the WAD cyanide level is always greater than or equal to the free cyanide concentration.</u>***

►Each of these forms of cyanide has specific analytical methodologies for its sample preparation and measurement, and the relationship between these forms must be understood when analyzing cyanide-containing solutions.

http://technology.infomine.com/reviews/Cyanide (You have to register to use this site)
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Free Cyanide:

►HCN and CN^- in solution are classified as **free cyanide**.

► The ratio of HCN to CN^- in solution is influenced by the solution pH.

►*Methods used to separate and detect free cyanide should not alter the stability of weaker cyanide complexes,* or they may be included in the free cyanide result resulting in a higher value.

ASTM method uses pH to match that of the sample; between pH 6 and pH 8.

CATC, Available Cyanide, WAD Cyanide

These are measurements of cyanides that are considered **bioavailable**.

Cyanide Amenable to Chlorination (CATC) includes the toxicologically and environmentally important forms of cyanide, CATC includes free cyanide and moderately and weakly complexed metal-cyanides.

Cyanides Amenable to Chlorination (CATC)

To determine CATC, a sample is split into two portions, with one portion tested for **total cyanide** and the second portion treated with calcium hypochlorite (to destroy cyanide) prior to a total cyanide test.

“Cyanides Amenable to Chlorination” refers to complexes that will break apart and oxidize when exposed to chlorine at high pH. (The final result consists of free cyanide and weak acid dissociable cyanide complexes).

The difference from total cyanide contents constitutes CATC cyanide; CATC is a test of how effective chlorination is in removing cyanide

Weak Acid Dissociable Cyanide (WAD CN)

► WAD cyanide includes species that will release cyanide at a moderate pH of 4.5 such as HCN(aq) and CN-, the majority of Cu, Cd, Ni, Zn, Ag, Hg, complexes and others with similar low dissociation constants, as well as free cyanide.

► The WAD CN final result is equivalent to Available Cyanide and CATC

Available Cyanide

Available Cyanide is equivalent to CATC and WAD Cyanide

No high temperature, long distillation. Ligand exchange reagents are added off-line at room temperature

Fewer interferences, faster than traditional WAD or CATC methods.

Available and WAD Cyanide do not require 2 distillations per sample as CATC does.

Total Cyanide

Total Cyanide includes:

All free cyanide, all dissociable cyanide complexes (i.e.WAD Cyanide),and all strong metal cyanide complexes including ferro-cyanide $Fe(CN)6^{-4}$, ferri-cyanide $Fe(CN)6^{-3}$, and portions of hexacyanocobaltate $Co(CN)6^{-3}$ as well as portions of cyanide compounds containing gold and platinum.

TOTAL CN

Free Cyanide, acid-dissociale cyanides, and strong metal-cyano complexes such as ferri and ferro cyanide, hexacyanocobaltate, and gold and platinum cyanides

WAD CN

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FREE CN

HCN and CN^- in solution

Only the compounds cyanate (CNO-) and thiocyanate (SCN-) are excluded from the definition of total cyanide.

SAMPLE PREPARATION FOR THE MEASUREMENT OF CYANIDE

Distillation

Most cyanide measurements require distillation prior to the measurement.

The purpose of distillation is simple: **Sample clean-up**. (in the case of cyanide, there can also be digestion).

The distillation process transfers the analyte from the sample into a clean, reproducible solution, for more accurate measurement. In some cases, it can also provide sample concentration and reduction of interferences.

Sample Preparation for Cyanide Analysis

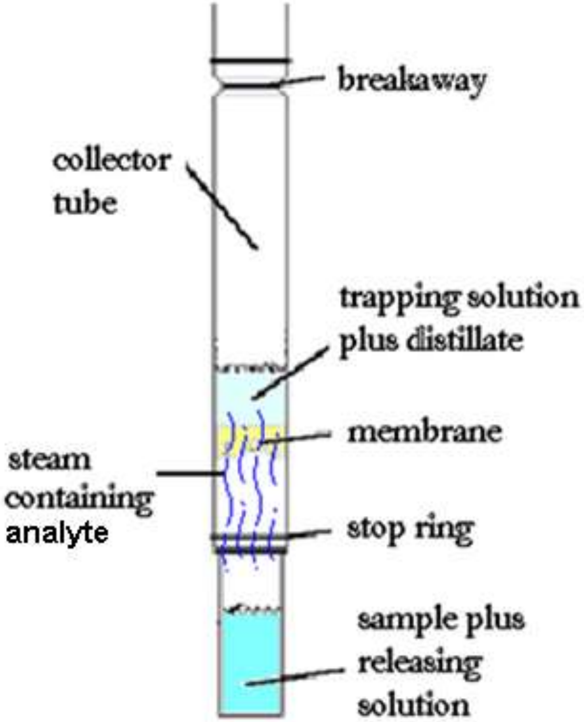
Traditional Macro-Distillation
Apparatus (missing heating mantle)

Sample clean-up by distillation had historically been performed in large volume, macro or midi-distillation glassware.

Traditional Midi-Distillation Apparatus

There are now disposable distillation devices, and in-line distillation methods available.

MicroDist™



Distillation End

MicroDist is a disposable alternative for off-line distillation

The vapor condenses **above the membrane** to form droplets, which pool on top of the membrane.

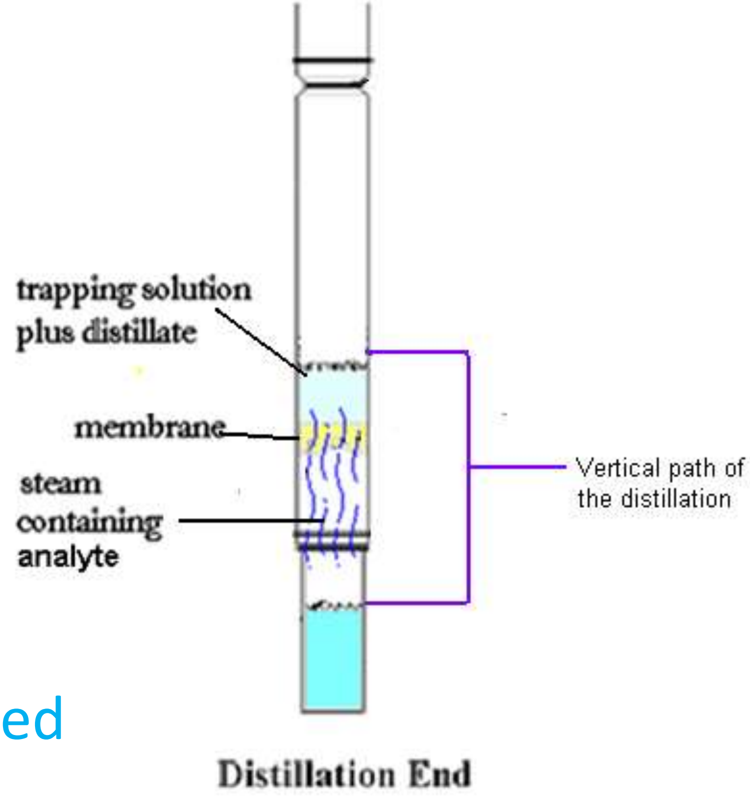
In the case of cyanide, the vapor is trapped in an NaOH solution.

MicroDist^{TM}

The **physical separation of distilling sample and distillate** by the hydrophobic membrane allows a very short vertical path for the distillation

➡ The liquid phase cannot pass back through the hydrophobic membrane.

The distillate can then be measured on an FIA or other automated system, or manually



Distillation End

In-line Distillation

Although the completely automated methods (in-line sample preparation) were common outside the US (EU and China in particular), USEPA only began to fully allow in-line sample preparation methods as equivalent for NPDES reporting beginning in 2007.

In-line sample preparation can include distillation across a semi-permeable, hydrophobic membrane as well

Sample Preparation for Cyanide Analysis

Although it is allowed for NPDES reporting, In-line distillation is not the best approach for all samples.

➡ Off-line sample preparation is best when samples contain particulates that must be included in the analysis, when contaminated soil or sludge is being tested, or for other difficult matrices such as animal tissue.

In-line Sample Preparation Methods

In-line distillation/digestion can be a very cost effective, less labor intensive, and less time intensive method for cyanide analysis.

In order to speed up the process over an off-line digestion/distillation, UV light is included in the process

Lower energy UV lamps are used so that thiocyanate is NOT recovered. The light energy is not great enough to break apart the SCN^-. Because SCN^- itself is not volatile, it does not pass through the gas diffusion membrane.

In-line Digestion/Distillation

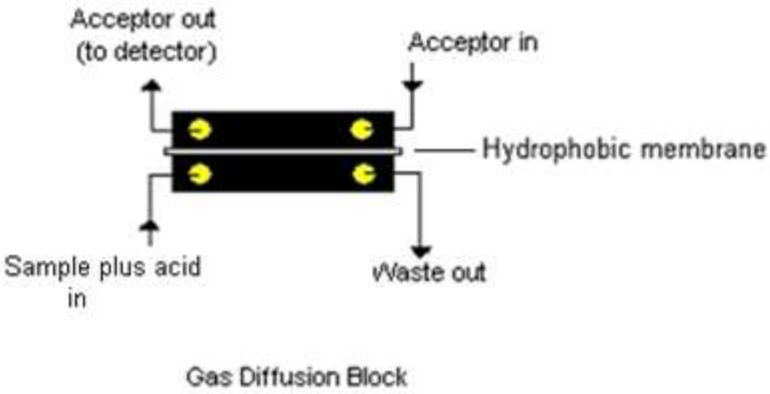
There are similarities between the in-line distillations, and the way that MicroDist^{TM} works.

In order to speed up the process over an off-line digestion/distillation, UV light is included in the process

Lower energy UV lamps are used so that thiocyanate is NOT recovered. The light energy is not great enough to break apart the SCN^-. Because SCN^- itself is not volatile, it does not pass through the gas diffusion membrane.

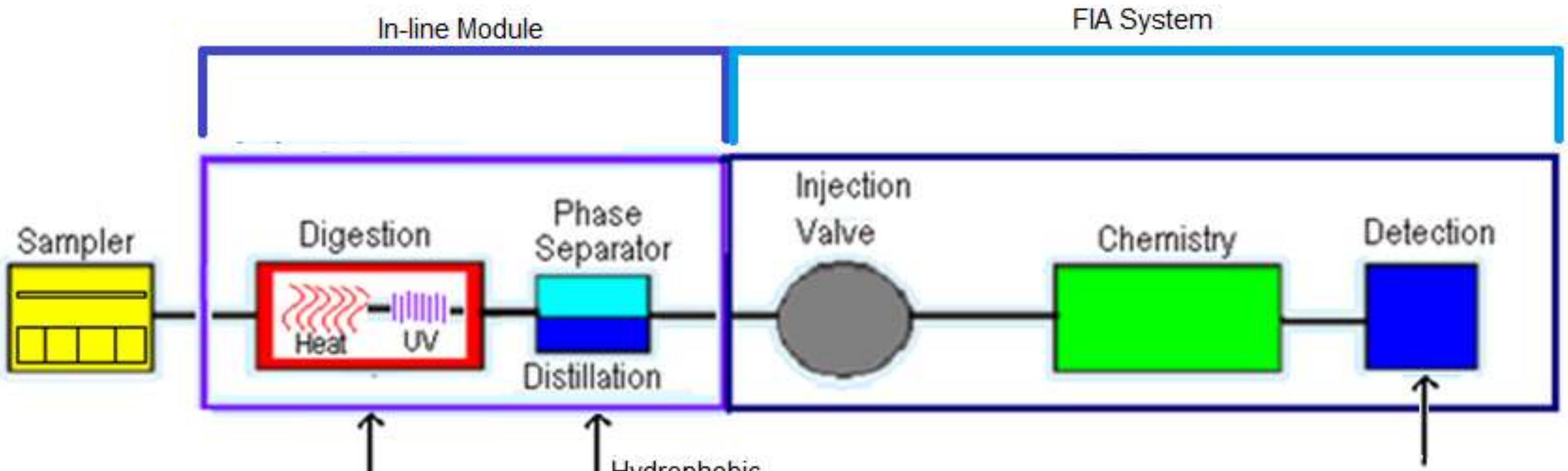
In-line Distillations for Cyanide

Like the MicroDist^{TM} distillation system, Lachat's in-line distillation methods also work by providing a physical separation of the distilling sample and distillate using a semi-permeable, hydrophobic membrane:



Also, as in the case of the MicroDist^{TM}, the liquid phase cannot pass back through the hydrophobic membrane.

Basic Overview of In-line Sample Preparation Methods:



Heat is used in Traditional methods.

ASTM D7511-09 Uses only the lamp no heating

Hydrophobic membrane for separation

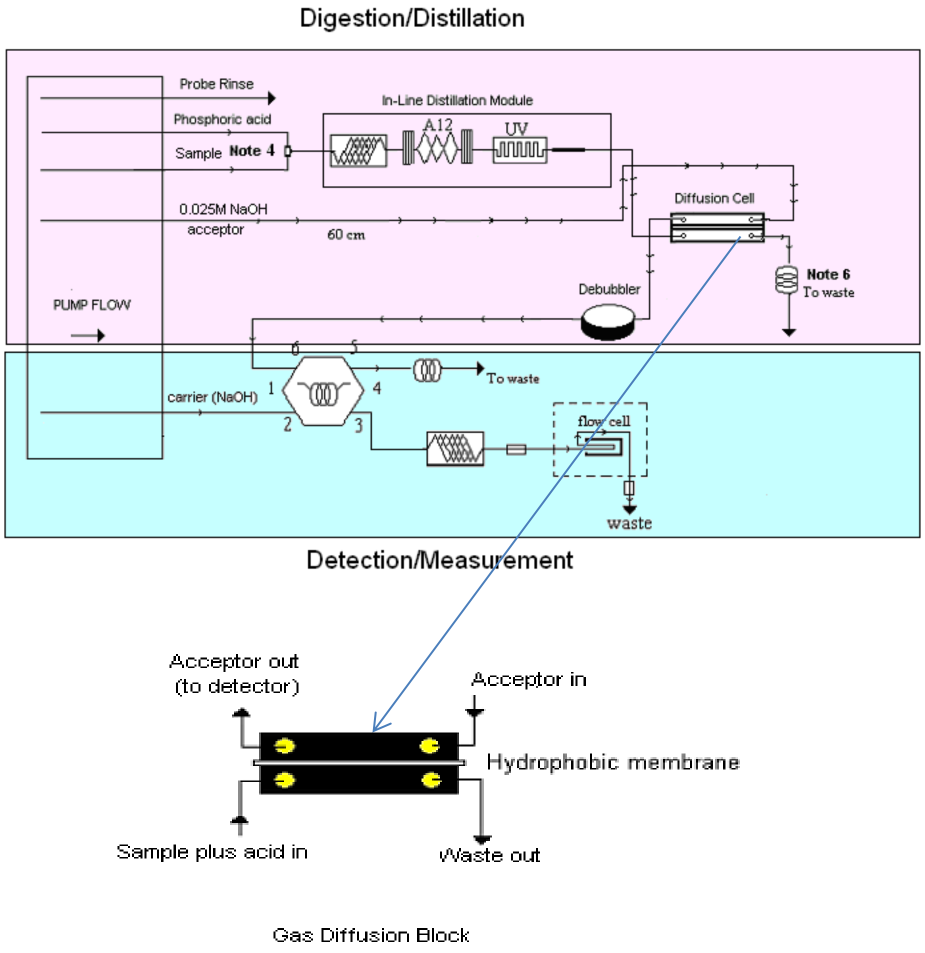
Colorimetric or Amperometric

In-line Distillation

- Total Cyanide: sample is mixed with dilute acid, in-line, may be heated, and then exposed to UV light

- CN^- in solution becomes $HCN_{(g)}$

- $HCN_{(g)}$ passes through a hydrophobic membrane, and is trapped in dilute NaOH



Sample Preparation for Cyanide

Following the chosen method of sample preparation, cyanide can be determined through colorimetric or amperometric methods.

(There are also cyanide ISE's available).

There are <u>many</u> ways of measuring cyanide once it is in a free form.

Colorimetric Analysis of Cyanide

- Pyridine-barbituric acid: This is the USEPA approved colorimetric assay and is used in methods 10-204-00-1-A and 10-204-00-1-X for example.

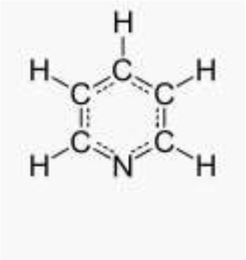
- Isonicotinic/Barbituric acid reagent. This color reagent is used primarily in the Chinese market. **Its primary advantage is that it does not use pyridine.** Methods10-204-00-1-G and 10-204-00-4-B use these reagents

- Isonicotinic/1,3,dimethyl barbituric acid To meet the ISO standard (14443) 10-204-00-2-H uses these reagents.

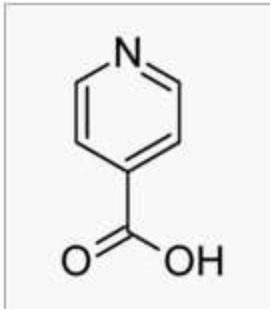
  (In the US, substituted barbituric acid compounds are more difficult to use due to DEA regulations, although some labs also run into difficulty with unsubstituted barbituric acid).

- Pyridine/pyrazolone: not EPA accepted. Required in Japan.

Colorimetric Analysis of Cyanide



Pyridine



Isonicotinic acid[

Isonicotinic acid is a carboxylated pyridine.

Amperometric Detection

Amperometric Detection: Lachat has a total of 6 cyanide methods that utilize amperometric detection. Many are equivalent under the MUR. The method for Available Cyanide is USEPA Accepted for Drinking water as well.

Digestion is done using pH and UV light.

Less interference issues, especially in the case of Total Cyanide.

Equivalent methods use this detection for **ASTM D7511-09** (total CN) **D6888-09** (Available CN) and **D7237-10** (Free CN), as well as following the MicroDist distillation (**D7284-08**)

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Amperometric Detection

Amperometric detection is an electrochemical method.

This approach requires fewer reagents; and no barbituric acid or pyridine are required

Cyanide in the sample is separated by ligand exchange, digestion/ distillation followed by gas diffusion, or just gas diffusion prior to detection.

In Amperometric Detection, the current generated is proportional to the concentration of the species generating the current

Electrochemical detection can also be thought of as electrolysis at a fixed point in a flowing stream, in this case the flowing solutions used for the FIA method in question.

The zone within this flowing solution containing the analyte becomes a thin film as it passes through the detector.

As the sample slug passes through the detector, a change in current occurs, with current being proportional to concentration.

The electrode in this case functions like a chemical reagent.

In the case of cyanide, no potential is applied.

CN- ions are electron donors giving a positive signal

Colorimetric Analysis of Cyanide

Lachat Instruments has available methods utilizing these chemistries, covering Free, Total, and WAD Cyanide as well as Thiocyanate. Total cyanide methods can include off-line (macro- or Microdist^{TM} distillations) or in-line digestion/distillation.

Ultra High Throughput (120 samples and standards per hour) and Ultra Low Flow methods (reagent volumes similar to Discrete Instruments and 60 samples and standards per hour) are available.

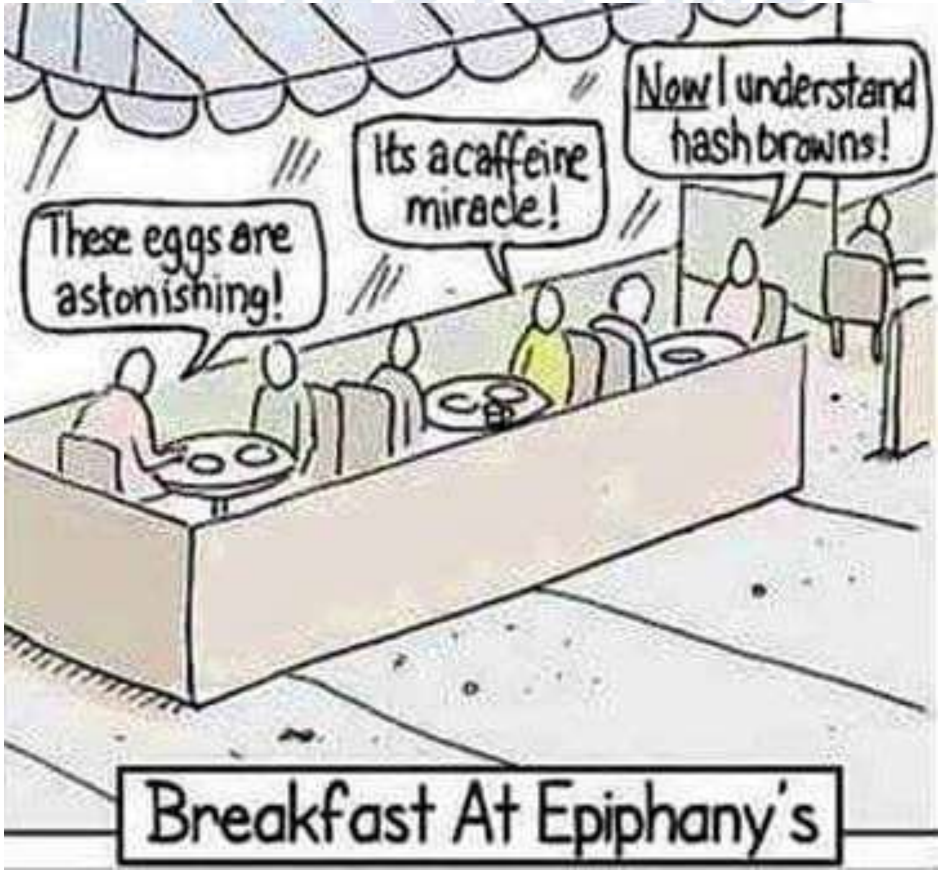
Both suites of methods were designed to decrease reagent use, and they are compliant with the March 2007 MUR; in addition, the high throughput method is EPA accepted under NPDWR.

Lachat Cyanide Methods

Method Number	USEPA NPDES	USEPA NPDWR	USEPA Method
Cyanide			
10-204-00-1-A#	NPDES Accepted	Accepted	
10-204-00-1-B	Equivalent		335.4
10-204-00-1-F	Equivalent		335.4
10-204-00-1-X	Approved	Approved	Promulgated method
10-204-00-1-X2^#	Equivalent	Accepted	
10-204-00-2-C[1]^	Equivalent		
10-204-00-2-D[1]^	Equivalent		
10-204-00-2-E[1]^	Equivalent		
10-204-00-5-A^#	Equivalent	Accepted	ASTM Method D6888-04
10-204-00-5-C	Equivalent		ASTM Method D7237-10
10-204-00-5-D^	Equivalent		ASTM Method D7511-09
80-204-00-1-A^	Equivalent		335.4
80-204-00-1-X^	Equivalent		10-204-00-1-X

[1] EPA has revised the language at (b)(4)(T) be **more specific with respect to the use of gas diffusion across a hydrophobic semi-permeable membrane,** to separate the analyte of interest from the sample matrix in place of manual or automated distillation for the analysis of certain analytes.

QUESTIONS?


These eggs are astonishing!
Its a caffeine miracle!
Now I understand hash browns!
Breakfast At Epiphany's